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Title

A Quantitative Study of Solutions Through Gas Chromatography

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I. Administration of the Contract

A. Personnel

No new personnel have been added to the project. The appointment of a Graduate Assistant under the contract was again postponed, but it is hoped that a qualified Graduate Assistant will be available to work over the summer.

B. Activity since last report (October 29, 1964)

The gas chromatograph is now operable, after the delays recounted in the last report. Experiments are now in progress to define the conditions of optimum performance for the purposes of the investigation, as discussed in the previous reports (see p. 4 of the October report).

A stipulation that the cost of the components for our gas chromatograph should not exceed \$2,707 was made in the letter from Dr. Smull (June 10, 1964) giving permission to purchase components, some from overseas, instead of the commercial gas chromatograph unit originally contemplated. Our records show that the parts referred to cost approximately \$2,350. Brokerage fees and other expenses add around \$200. The cost was thus under the maximum stipulated, and represents a saving of approximately \$950 over the allotment of \$3,500 for the gas chromatograph. In addition, we believe we have obtained the superior temperature and flow control which we were seeking.

During the period in which experimental work was hampered by the unfortunate delays in receiving essential parts, a good deal of attention was given to the matter of virial coefficients. The object was to explore means of determining them rapidly (in particular with reference to the interaction second virial coefficient, B_{12}), and to consider their significance in the study of molecular interactions.

C. Projected activity on the project.

In the next six months a great deal of experimental data should come from the work with the gas chromatograph. The analysis and interpretation

of the data is expected to be rewarding. As the previous reports explained, the technic of factor analysis will play an important part in the analysis of the data, and it should be mentioned that some studies for the purpose of making the computations of factor analysis easier to manage and apply are being successfully pursued in the Chemistry Department (although not under this project) in cooperation with the Stevens Computer Laboratory.

Reprints of the article "Compressibility Factor for Nonideal Carrier Gases in Gas Chromatography," by D. E. Martire and D. C. Locke (Analytical Chem., 37, 144 (1964).) are enclosed with this report. As mentioned in our October report, this work was initiated prior to NASA support of the project.

Dr. Locke has completed a manuscript, "Gas-Solid Chromatography With Real Carrier Gases," which is attached to this report. In a revised and abbreviated version, this work will soon be submitted for publication to the Journal of Physical Chemistry.

In recent months a search has been made for measurements of second virial coefficients which would give independent checks on the values which can be extracted from gas chromatographic data. The study of these values is a part of the objective of this project. Where direct measurements have not been made, it is necessary to calculate the second virial coefficients from other data. The methods involve, besides the use of P-V-T data, heat of vaporization vapor pressure data, heat capacity data, sound velocity data, or refractive index measurements on the gas phase. Unfortunately, there have been few direct measurements made on interaction second virial coefficients. Recourse must be made generally either to gross approximations, or to measurements on mixtures of gases over a range of concentrations. We suspect that the simplest approach is through the use of refractive index measurements, following the method of Guggenheim and Ashton (Proc. Phys. Soc., B69, 693 (1956)). Calculations are being undertaken to apply this method to available data.

Compressibility Factor for Nonideal Carrier Gases in Gas Chromatography

SIR: The recent work of Desty, *et al.* (5) has demonstrated that the carrier gas in gas chromatography cannot be considered as an ideal, non-interacting, neutral fluid whose only action is to transport the solute vapors through the column. When accurate thermodynamic measurements are attempted using gas chromatography, it is necessary to correct for the non-ideality of the gas phase (1, 5, 6). One criticism which might still be leveled at experimental studies in which non-ideal gas behavior has been considered (1, 5, 6) is that mean column pressures and corrected retention volumes were calculated using the Martin and James compressibility factor (4, 8) which was derived for ideal gases.

This communication describes a method for calculating mean column pressures for real carrier gases, where gas phase interactions can cause appreciable deviations from ideality. It is shown that the effect of nonideality on mean column pressure is small, and can be neglected in most cases except where the highest accuracy is required.

Let us first review the derivation of the Martin and James factor for ideal gases, for comparison with the expression for real carrier gases. The carrier gas velocity, u , is related in a general way to the pressure drop across the column according to

$$u = -c dp/dx \quad (1)$$

where c is the column permeability constant and p is the column pressure at any point, x , down the column. For an ideal gas, whose equation of state is $PV = nRT$, it is readily shown that the mass flow rate pu is given by

$$pu = p_0 u_0 = \frac{m}{M} RT = \text{constant} \quad (2)$$

at any point down the column. In this equation, m is the molar flow rate (moles of carrier gas/unit time), M is the molecular weight of the carrier gas, R is the gas constant, T is the absolute column temperature, and the subscripted zeroes refer to column outlet conditions. The mean column pressure is defined by

$$\bar{P} = \frac{\int_0^L p dx}{\int_0^L dx} \quad (3)$$

Substituting Equations 1 and 2 into 3, changing variables from position to pressure, and integrating,

$$\bar{P} = \frac{\int_{p_0}^{p_i} -\frac{cp^2 dp}{p_0 u_0}}{\int_{p_0}^{p_i} -\frac{cp dp}{p_0 u_0}} = \frac{\int_{p_0}^{p_i} p^2 dp}{\int_{p_0}^{p_i} p dp}$$

$$\bar{P} = \frac{1/3 (p_i^3 - p_0^3)}{1/2 (p_i^2 - p_0^2)} = \frac{2}{3} p_0 \left(\frac{a^3 - 1}{a^2 - 1} \right) = p_0/j \quad (4)$$

where a is the ratio of inlet to outlet pressures, p_i/p_0 , and j is the Martin and James compressibility factor.

For real gases, we choose a simple two-term virial equation of state,

$$PV = nRT + nB_{11}P \quad (5)$$

where B_{11} is the second virial coefficient of the carrier gas, representing interactions occurring between the carrier gas molecules. Equation 2 then becomes

$$p \left(u - \frac{m}{M} B_{11} \right) = \frac{m}{M} RT \quad (6)$$

Thus

$$u = \frac{m}{M} \left(\frac{RT}{p} + B_{11} \right) = -cdp/dx \quad (7)$$

Rearranging Equation 7,

$$dx = -\frac{cM}{mRT} \left(\frac{p dp}{1 + \frac{B_{11}p}{RT}} \right) \quad (8)$$

For the mean column pressure, we now have

$$\bar{P} = \frac{\int_{p_0}^{p_i} \frac{p^2 dp}{1 + \frac{B_{11}p}{RT}}}{\int_{p_0}^{p_i} \frac{p dp}{1 + \frac{B_{11}p}{RT}}} \quad (9)$$

Integration yields:

$$\bar{P} = \frac{\left(\frac{RT}{B_{11}} \right)^3 \left[\frac{1}{2} \left(\frac{B_{11}}{RT} \right)^2 (p_i^2 - p_0^2) + \frac{B_{11}}{RT} (p_i - p_0) + \ln \left(\frac{1 + B_{11} p_i / RT}{1 + B_{11} p_0 / RT} \right) \right]}{\left(\frac{RT}{B_{11}} \right) \left[(p_i - p_0) - \left(\frac{RT}{B_{11}} \right) \ln \left(\frac{1 + B_{11} p_i / RT}{1 + B_{11} p_0 / RT} \right) \right]} \quad (10)$$

Expansion of the \ln terms in a Maclaurin series and algebraic simplification of the result leaves:

$$\bar{P} = \frac{1/3 (p_i^3 - p_0^3) - 1/4 \left(\frac{B_{11}}{RT} \right) \times 1/2 (p_i^2 - p_0^2) - 1/3 \left(\frac{B_{11}}{RT} \right) \times (p_i^4 - p_0^4) + \dots}{(p_i^3 - p_0^3) + \dots} \quad (11)$$

In terms of $a = p_i/p_0$, and neglecting higher terms in the expansion,

$$\bar{P} = \frac{1/3 (a^3 - 1) - 1/4 \left(\frac{B_{11}}{RT} \right) (a^3 p_i - p_0) [1/(2p_0)] (a^2 - 1) - 1/3 \left(\frac{B_{11}}{RT} \right) (a^3 - 1)}{[1/(2p_0)] (a^2 - 1) - 1/3 \left(\frac{B_{11}}{RT} \right) (a^3 - 1)} \quad (12)$$

For $p_0 = 1.000$ atm., Equation 12 becomes numerically equivalent to

$$\bar{P} = \frac{1/3 (a^3 - 1) - 1/4 \left(\frac{B_{11}}{RT} \right) (a^4 - 1)}{1/2 (a^2 - 1) - 1/3 \left(\frac{B_{11}}{RT} \right) (a^3 - 1)} \quad (13)$$

Thus, for a given inlet and outlet pressure, the mean column pressure will depend upon the nature of the carrier gas. The effect of nonideality will be greatest for low column temperatures and high inlet pressures. For ideal gases, $B_{11} = 0$, Equation 12 reduces to Equation 4.

To use this correction, values of B_{11} at the column temperature are needed. If it can be assumed that the carrier gas molecules conform to the corresponding states principle, second virial coefficients can be calculated from an empirical Beattie-Bridgeman (2)-type formula shown by Guggenheim and McGlashan (7) to be applicable over a wide range of temperatures:

$$\frac{B_{11}}{V^*} = 0.461 - 1.158 \left(\frac{T^*}{T} \right) - 0.503 \left(\frac{T^*}{T} \right)^3 \quad (14)$$

where V^* and T^* are the critical [or characteristic (?)] volume and temperature of the carrier gas, respectively. Values of B_{11} at 25° C. for several of the common carrier gases are presented in Table I.

Mean column pressures calculated from Equation 13 over a range of p_i/p_0 ratios normally encountered in gas chromatography for several of the most common carrier gases are presented in Table II.

These calculations were made for $p_0 = 1.000$ atm. and a column temperature of 25° C. As anticipated, the effect is small, increasing with increasing p_i/p_0 ratio and carrier gas

nonideality; for CO_2 carrier gas at $p_i/p_0 = 5.0$, only a 0.16% error is incurred by using Equation 4 to calculate the mean column pressure rather than Equation 12. Thus, except in unusual circumstances or where the highest accuracy is desired, this correction need not be applied. Since the mean column pressure depends upon a , B_{11} , and T , it would be inconvenient to prepare extensive tables of these correction factors, as have been prepared for the Martin and James j factor (3).

It should be noted that as the mean column pressure becomes very large, higher terms will be needed in the equation of state, Equation 5. Such a circumstance, however, would be rare in gas chromatography and is therefore not considered here.

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Table I. Critical Constants and Calculated Second Virial Coefficients for Carrier Gases at 25° C.

Carrier gas	(cm. ³ -mole ⁻¹)		B_{11}^c
	T^{*a}	V^{*b}	
He	7.66° K.	33.7 cc.	+15 cc.-mole ⁻¹
H ₂	43.4	50	+15
N ₂	126.0	90.2	-6
Ar	150.7	75.3	-14
CO ₂	-124 ^d
CH ₄	190.3	98.8	-40
CO	133.0	93.2	-9
Ne	44.8	41.7	+12
O ₂	154.3	74.5	-16

^{a,b} Data given in (7).

^c Calculated from Equation 14.

^d Value given in (5).

Table II. Mean Column Pressures Calculated from Equation 13 for $p_0 = 1$ atm. at 25° C.

Carrier gas	B_{11} cc./mole	a			
		1.5	2.0	2.5	3.0
He, H ₂	+15	1.26665	1.55551	1.85703	2.16648
Ideal	0	1.26667	1.55556	1.85714	2.16667
N ₂	-6	1.26667	1.55558	1.85719	2.16674
Ar	-14	1.26668	1.55560	1.85724	2.16684
CO ₂	-124	1.26677	1.55596	1.85803	2.16820
Maximum % difference from ideal		0.01	0.03	0.05	0.07

Carrier gas	B_{11} cc./mole	a			
		3.5	4.0	4.5	5.0
He, H ₂	+15	2.48119	2.79959	3.12067	3.44375
Ideal	0	2.48148	2.80000	3.12121	3.44444
N ₂	-6	2.48160	2.80016	3.12143	3.44472
Ar	-14	2.48175	2.80038	3.12172	3.44509
CO ₂	-124	2.48382	2.80330	3.12563	3.45010
Maximum % difference from ideal		0.09	0.12	0.14	0.16

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GAS-SOLID CHROMATOGRAPHY WITH REAL CARRIER GASES

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Introduction

Gas-solid chromatography (GSC) has been used for the separation of gaseous mixtures somewhat longer than gas-liquid chromatography (GLC). However, being restricted mainly to the analysis of the fixed gases and simple organic compounds, the study of GSC became submerged in the deluge of theory and application following the advent of GLC in 1952. More recently, however, renewed interest has arisen in linear elution GSC.

Increasing attention has been paid to the technique at recent symposia.¹¹ Purnell,³³ whose text is a sourcebook of ideas, has suggested that the technique will become increasingly effective and attractive as new developments arise in the experimental aspects of GSC. The broad chromatographic interests of Giddings¹² have recently returned to the theory and analytical potential of GSC. The introduction of new adsorbents with excellent chromatographic properties, such as fibrillar boehmite,²³ and the use of open tubular adsorption columns^{5,30,32} offer new areas for exploration. Sensitive ionization detectors permit the use of samples sufficiently small to insure operation in the linear (Henry's law) portion of the adsorption isotherm, with the elimination of problems attending nonlinear adsorption.

In this paper, several systems defined in terms of the observed sample and carrier gas adsorption isotherms are considered. Quantitative

predictions are made as to the effect of gas phase nonideality on the retention behavior of adsorbates in GSC. As in GLC,⁹ for a given carrier gas in the simpler adsorption systems, absolute sample retention is linearly related to the mean column pressure; at constant pressure, retention decreases with increasing nonideality of the gas phase. It is anticipated that GSC will provide a simple, reasonably accurate method for the determination of the second virial coefficients which characterize these gas phase imperfections. The utilization of small changes in retention with mean column pressure or carrier gas nonideality may have important analytical consequences for the resolution of difficulty separable mixtures. Since the fundamental distribution coefficient is proportional to the adsorption constant of the sample, it follows that GSC offers a means for obtaining information about gas-solid interactions. It is suggested that GSC has considerable potential for the separation of isotopes.

Theory

From the basic theorems of chromatography, it can be shown that the retention time, t_r , of some component of interest (the adsorbate) is related to its adsorption partition ratio, k_a , by

$$t_r = (L/u) (1 + k_a) = t_m (1 + k_a) \quad (1)$$

where L is the column length, u is the carrier gas velocity, t_m is the retention time of an unadsorbed component, and k_a is defined by

$$k_a = \frac{\text{amount of component in the adsorbed phase}}{\text{amount of component in the gas phase}} \quad (2)$$

The more fundamental adsorption distribution coefficient, K_a , which is defined here as

$$K_a = \frac{\text{number of moles of component adsorbed per unit weight of adsorbent}}{\text{number of moles of component in the gas phase per unit volume of gas phase}} \quad (3)$$

is related to the partition ratio according to

$$K_a = k_a (V^g/w_a) \quad (4)$$

where V^g is the interstitial volume of the column, the retention volume of an unadsorbed component, and w_a is the weight of adsorbent in the column. Note that K_a has units of cc/g of adsorbent, while k_a is dimensionless. We could have as easily defined K_a in terms of the number of moles of component adsorbed per unit area of adsorbent. In this case K_a would have dimensions of cm. However, the weight of adsorbent is more readily measured than its surface area. In any case, the final results will differ only by a constant, and as will be seen, we will usually need to know both the surface area and the weight of adsorbent present.

k_a is determined using equation (1). K_a can be obtained from equation (4) and is related to the corrected retention volume by

$$V_R^0 = V^g + K_a w_a \quad (5)$$

and to the heat of adsorption, ΔH_a , by

$$K_a = c \exp(-\Delta H_a/RT) \quad (6)$$

In this paper we shall be mainly concerned with the effect of mean column pressure and gas phase nonideality on retention (K_a or k_a). The development used here relies heavily on the similar treatment of GLC by Luckhurst, who with Desty et al.⁹ considered this effect in gas-liquid

chromatographic systems. The case of GSC, however, is slightly more complicated; both the component of interest and the carrier gas may adsorb, and each may follow a different adsorption isotherm. Furthermore, the carrier gas may behave ideally for all practical purposes, as is effectively the case with helium at high temperatures, but the adsorbate vapors may deviate appreciably from ideal behavior. It is apparent that several distinct situations need to be considered.

It will be assumed in most cases that the adsorbate obeys Henry's law for adsorption, i.e., that the amount of component present is so small that its adsorption isotherm is linear. Experimentally, this qualification is easily met since very small samples can be used in conjunction with sensitive ionization detectors or microvolume/thermal conductivity cells. The carrier gas may not be adsorbed, or it may follow a linear or a Langmuir-type adsorption isotherm, depending upon the experimental conditions, the characteristics of the adsorbent, and the nature of the carrier gas.

Situations involving multimolecular adsorption will not be considered in this paper. Although mean column pressures may be as large as several atmospheres, normal operating temperatures are considerably higher than the critical temperatures of the usual carrier gases. Thus carrier gas adsorption usually will occur only to an extent which can be described by a linear or Langmuir-type isotherm.

It will be necessary in all cases to consider that second order adsorbed phase interactions are negligible. This assumption will be valid if we restrict our attention to situations where only very small quantities of sample are present. In such cases, lateral interactions between adsorbates and interactions between the bulk gas and the adsorbed species will be negligible.^{1,19} This is an important consideration if

experimental deviations from ideal behavior are reflections of gas-phase interactions only.

The first case to be considered (Case I) is the simplest: the carrier gas is not adsorbed, the adsorbate follows a linear isotherm, and the gas phase is considered ideal. In practice, such a situation could be approximated with very small samples of simple adsorbates, He carrier gas, and moderately high column temperatures. Letting n_2^a be the number of moles of component adsorbed and n_2^g be the number of moles of component in the gas phase,

$$K_a = \frac{n_2^a/w_a}{n_2^g/V^g} \quad (7)$$

Following Barker and Everett's derivation,¹ we find an expression of Henry's adsorption law:

$$n_2^a = k_H A p_2^g \quad (8)$$

where k_H (in mole-atm⁻¹-cm⁻²) is the adsorption constant, a function of the gas-solid interaction potential energy; A is the surface area of the adsorbent present; and p_2^g is the partial pressure of sample component of interest above the adsorbent. Adsorption is linear with the quantity of sample present. For ideal gases,

$$\frac{n_2^g}{V^g} = \frac{p_2^g}{RT} \quad (9)$$

Thus

$$K_a = \frac{k_H A p_2^g RT}{w_a p_2^g} = k_H A RT/w_a \quad (10)$$

In terms of the adsorption partition ratio,

$$k_a = K_a (w_a/V^g) = k_H A RT/V^g \quad (11)$$

k_a is dimensionless, as it should be.

The next situation, Case II, is the same as Case I except that the gas phase behaves nonideally. These conditions may be experienced with say H_2 carrier gas and a low activity adsorbent (graphitized carbon black, for example²⁵) at moderate column temperatures. The adsorbate follows a linear isotherm but the carrier gas is not adsorbed. For real gases, we have in place of equation 8,

$$n_2^g = k_H A f_2^g, \text{ or } \ln n_2^g = \ln k_H A + \ln f_2^g \quad (12)$$

where f_a^g is the fugacity of the adsorbate above the adsorbent, related¹⁷ to the partial pressure according to

$$\ln f_2^g = \ln p_2^g + (\bar{P}/RT) \left[B_{22} - (1 - y)^2 (B_{11} - 2B_{12} + B_{22}) \right] \quad (13)$$

In this equation, y is the mole fraction of adsorbate vapor in the gas phase, \bar{P} is the mean column pressure, B_{11} and B_{22} are the second virial coefficient of the pure carrier gas and adsorbate vapors, respectively, and B_{12} is the interaction second virial coefficient, characterizing the interactions between the carrier gas and the sample vapor molecules, at T °K. B_{12} is given by the expression²⁷ relating B_{11} and B_{22} to the second virial coefficient of a gaseous mixture, B_m :

$$B_m = y^2 B_{22} + 2y(1 - y)B_{12} + (1 - y)^2 B_{11} \quad (14)$$

Since

$$y = n_2^g / (n_2^g + n^g) = p_2^g / (p_2^g + p_1^g) = p_2^g / \bar{P} \quad (15)$$

where n^g is the number of moles of gas phase present in the column, and p_1^g is the partial pressure of carrier gas present, and since

$$\bar{P} v^g = (n_2^g + n^g) (RT + B_m \bar{P}) \quad (16)$$

equation 7 becomes

$$\begin{aligned} K_a &= (n_2^a/w_a) \left[v^g/y(n_2^g + n^g) \right] \\ &= (n_2^a/w_a) (\bar{P}/p_2^g) \left[\frac{RT}{\bar{P}} + y^2 B_{22} + 2y(1-y)B_{12} + (1-y)^2 B_{11} \right] \end{aligned} \quad (17)$$

Combining equations 12, 13, 15, and 17,

$$\begin{aligned} \ln K_a &= \ln (k_H \bar{A} \bar{P}/w_a) + \ln \left[\frac{RT}{\bar{P}} + y^2 B_{22} + 2y(1-y)B_{12} + (1-y)^2 B_{11} \right] \\ &\quad + \frac{\bar{P}}{RT} \left[B_{22} - (1-y)^2 (B_{11} - 2B_{12} + B_{22}) \right] \end{aligned} \quad (18)$$

For very small samples, $y \rightarrow 0$. Then after rearranging equation 18, expanding the resulting term $\ln (1 + B_{11} \bar{P}/RT)$, and neglecting all but first order terms in the expansion,

$$\ln K_a = \ln (k_H A RT/w_a) + 2B_{12} \bar{P}/RT \quad (19)$$

A plot of $\ln K_a$ vs \bar{P} should be linear, with a slope of $2B_{12}/RT$ and an intercept identical to equation 11.

Another case of lesser importance might also be considered. In Case III, the carrier gas closely approximates ideal behavior while the adsorbate vapors are thermodynamically imperfect. Such a circumstance might effectively arise if He were used as a carrier gas at high temperatures. Equation 16 now becomes

$$\bar{P} v^g = (n_2^g + n^g) RT \quad (20)$$

Assuming, ¹⁷ furthermore, that

$$\ln f_2^g = \ln p_2^g + \bar{P} B_{22}/RT \quad (21)$$

substitution into equation 7 gives

$$\ln K_a = \ln (k_H A RT/w_a) + \bar{P} B_{22}/RT \quad (22)$$

At ordinary operating temperatures, it is expected that most common carrier gases other than He or H₂ will adsorb on the active solid. One of the simpler nonlinear isotherms that a carrier gas might obey is that of Langmuir.²⁶ This treatment, a kinetic approach, assumes monolayer adsorption on a uniform, homogeneous surface. Lateral interactions between the adsorbed species are negligible. In GSC, where the carrier gas and the sample components may both be adsorbed, this requires that the only effect one adsorbate can have on the adsorption of another is to reduce the available surface area.³ Formulation of the Langmuir isotherm for mixed adsorbates thus proceeds as below:

Let θ_1 and θ_2 be the fractions of the surface of the adsorbent occupied by adsorbates 1 and 2, respectively. 1 refers to the carrier gas and 2 to the sample component under consideration. The fraction of free surface is therefore $(1 - \theta_1 - \theta_2)$. Since the rate of adsorption is proportional to the partial pressure of the adsorbate above the adsorbent, and to the available surface area of adsorbent, the rate of adsorption of 1 is $k_1 p_1^g (1 - \theta_1 - \theta_2)$, and that of 2 is $k_2 p_2^g (1 - \theta_1 - \theta_2)$, where the k_i 's are the respective rate constants. The desorption rates are $k_1^0 \theta_1$ and $k_2^0 \theta_2$, respectively, where the k_i^0 are new rate constants. At equilibrium, which we must assume is attained at all points down the column,

$$\begin{aligned} k_1 p_1^g (1 - \theta_1 - \theta_2) &= k_1^0 \theta_1 \\ k_2 p_2^g (1 - \theta_1 - \theta_2) &= k_2^0 \theta_2 \end{aligned} \quad (23)$$

Simultaneous solution of these equations yields

$$\theta_1 = \frac{b_1 p_1^g}{1 + b_1 p_1^g + b_2 p_2^g}$$

$$\theta_2 = \frac{b_2 p_2^g}{1 + b_1 p_1^g + b_2 p_2^g} \quad (24)$$

where the b_i are the ratio of the adsorption/desorption rate constants, the individual overall adsorption constants. If $p_2^g = 0$, or if $b_2 = 0$, i.e., in the absence of an adsorbing vapor, or in the presence of a non-adsorbing one, equation 24 reverts to the ordinary Langmuir isotherm for a single gas.

The number of moles of the i th gas adsorbed is, in Langmuir notation,

$$n_i^a = n_m^i \theta_i \quad (25)$$

where n_m^i is the number of moles of the i th component required to produce a monolayer on the surface of the adsorbent. Substitution of this into equation 24 gives

$$n_1^a = \frac{n_m^1 b_1 p_1^g}{1 + b_1 p_1^g + b_2 p_2^g}$$

$$n_2^a = \frac{n_m^2 b_2 p_2^g}{1 + b_1 p_1^g + b_2 p_2^g} \quad (26)$$

which define a Langmuir-type isotherm for mixed adsorption. Each gas decreases the amount of adsorption of the other according to the relative magnitudes of the $b_i p_i^g$ products.

In GSC, component 2, the adsorbate of interest, will in general obey a linear isotherm ($b_2 p_2^g \ll 1$). This situation produces limiting cases of equations 26:

$$\begin{aligned}
 n_1^a &= n_m^1 b_1 p_1^g / (1 + b_1 p_1^g) \\
 n_2^a &= n_m^2 b_2 p_2^g / (1 + b_1 p_1^g)
 \end{aligned}
 \tag{27}$$

The adsorption of the carrier gas (component 1) is not appreciably affected by the presence of component 2, but the linear adsorption of 2 is strongly influenced by the adsorption of carrier gas.

Solving equations 27 for $(1 + b_1 p_1^g)$ and equating,

$$n_2^a = c_1 n_1^a p_2^g / p_1^g \tag{28}$$

where $c_1 = n_m^2 b_2 / n_m^1 b_1$.

We can now consider Case IV, where the adsorbate obeys Henry's law, the carrier gas follows the Langmuir isotherm, and the gas phase behaves ideally. We can then identify p_1^g , the partial pressure of carrier gas, with the mean column pressure, \bar{P} , to a good approximation. From equations 7, 9, and 28,

$$K_a = c_1 n_1^a RT / \bar{P} w_a \tag{29}$$

From equation 27, using $p_1^g = \bar{P}$, we have

$$K_a = c_2 RT / w_a (1 + b_1 \bar{P}) \tag{30}$$

where $c_2 = c_1 n_m^1 b_1 = n_m^2 b_2$. Thus for these systems, the distribution coefficient should decrease with both increasing column pressure, as could be anticipated with a nonlinear isotherm, and with increasing strength of carrier gas adsorption (increasing b_1).

In Case V, the system under consideration is the same as Case IV except that all components in the gas phase behave imperfectly. Replacing partial pressures in equation 28 with fugacities, recalling the definition of y , the mole fraction of sample vapor in the gas phase, and substituting

into equation 7,

$$K_a = \frac{c_1 n_1^a v^g (f_2^g/f_1^g)}{w_a(n_2^g + n^g) (p_2^g/\bar{P})} \quad (31)$$

Proceeding as above (equations 13 and 16) and using (5)

$$\ln f_1^g = \ln \bar{P} + \bar{P}B_{11}/RT \quad (32)$$

we arrive at the desired result,

$$\ln K_a = \ln \left[c_2 RT/w_a (1 + b_1 \bar{P}) \right] + (\bar{P}/RT) (2B_{12} - B_{11}) \quad (33)$$

Under the proper circumstances, the adsorption of both the carrier gas and the sample may best be described by a linear isotherm. It will be noted that equation 30 is applicable to both linear and Langmuir adsorption, it being implicit in this equation that the only effect adsorption of one has on the other is to reduce the available surface area.

For the present case of linear adsorption of both sample vapor and carrier gas, $b_1 p_1^g$ and $b_2 p_2^g$ are both much less than 1, and the number of moles of carrier gas adsorbed is given by

$$n_1^a = n_m^1 b_1 p_1^g = n_m^1 b_1 \bar{P} \quad (34)$$

for very small samples. Thus $n_1^a/\bar{P} = n_m^1 b_1 = c'$, a new constant; since $c_1 c' = c_2$, we arrive at the expressions given in Table I for Cases VI and VII. Descriptions of the features of these systems are given in the Table.

Several more special cases might also be mentioned. The first of these, Case VIII, would apply if the sample component followed the Langmuir isotherm. In this case the carrier gas is not adsorbed, and the gas phase is ideal. From equation 26, since $b_1 = 0$,

$$n_2^a = n_m^2 b_2 p_2^g / (1 + b_2 p_2^g) \quad (35)$$

Then

$$K_a = n_2^a \sqrt{g}/n_2^g w_a = n_m^2 b_2 RT/w_a (1 + b_2 p_2^g) \quad (36)$$

Now the distribution coefficient is dependent upon the sample size (p_2^g), decreasing with increasing p_2^g . This is in agreement with experimental observations.²⁵ If the amount of adsorbate present is allowed to become very small, equation 36 reduces to the equivalent to equation 10.

Langmuir-type adsorption of the sample in conjunction with linear or Langmuir adsorption of the carrier gas leads to systems described by Cases IX and X, respectively. As in Cases VI and VII, equation 31 holds although n_1^a and n_2^a are now defined by equations 37 and 26 for the two respective situations:

$$\begin{aligned} n_1^a &= n_m^1 b_1 p_1^g / (1 + b_2 p_2^g) \\ n_2^a &= n_m^2 b_2 p_2^g / (1 + b_2 p_2^g) \end{aligned} \quad (37)$$

These results are also given in Table I.

Considerations similar to those employed above will allow assessment of the effect of gas phase nonideality on retention in these cases. A summary of the final results for K_a for the various cases considered is given in Table I.

Discussion

The equations in Table I are of interest from both a chromatographic and a thermodynamic point of view. Chromatographically, a prediction of the GSC behavior of several systems is presented. The equilibrium distribution coefficient per unit weight of adsorbent is proportional to the adsorption constant of the system, if the gas phase can be considered ideal, or proportional to this constant plus correction factors accounting for the non-ideality of the gas phase. It should be pointed out that the apparent

Summary of Expressions for K_a in Gas Solid Chromatography

TABLE I

Case	Adsorbate Isotherm	Carrier Gas Isotherm	Adsorbate Vapor	Carrier Gas	K_a	Eqn. No.
I	Linear	NA ¹	I ²	I	$K_a = k_H A RT/w_a$	10
II	Linear	NA	R ³	R	$\ln K_a = \ln (k_H A RT/w_a) + 2 B_{12} \bar{P}/RT$	19
III	Linear	NA	R	I	$\ln K_a = \ln (k_H A RT/w_a) + B_{22} \bar{P}/RT$	22
IV	Linear	Langmuir	I	I	$K_a = c_2 RT/w_a (1 + b_1 \bar{P})$	30
V	Linear	Langmuir	R	R	$\ln K_a = \ln c_2 RT/w_a (1 + b_1 \bar{P}) + (\bar{P}/RT)(2B_{12} - B_{11})$	33
VI	Linear	Linear	I	I	$K_a = c_2 RT/w_a$	
VII	Linear	Linear	R	R	$\ln K_a = \ln (c_2 RT/w_a) + (\bar{P}/RT)(2B_{12} - B_{11})$	
VIII	Langmuir	NA	I	I	$K_a = c_2 RT/w_a (1 + b_2 p_2^g)$	
IX	Langmuir	Linear	I	I	$K_a = c_2 RT/w_a (1 + b_2 p_2^g)$	
X	Langmuir	Langmuir	I	I	$K_a = c_2 RT/w_a (1 + b_1 p_1^g + b_2 p_2^g)$	

¹NA = Not Adsorbed

²I = Ideal Gas Phase

³R = Real, Nonideal Gas Phase

ideality or nonideality of such systems is to a large extent dependent on the accuracy of the measurements made. Analytically, most chromatographic systems behave ideally (in the thermodynamic sense) for all practical purposes. Those equations derived for the ideal gas phases are limiting cases for the real systems. For the cases with linear isotherms, but nonideal gas phases, $\ln K_a$ should show a slight but linear dependence on the mean column pressure for a given carrier gas; at constant pressure, $\ln K_a$ should decrease with increasing gas phase nonideality. For those systems with nonlinear carrier gas isotherms, this pressure dependence arising from vapor phase nonideality will be superimposed upon, and obscured by, the more direct, stronger pressure dependence exerted through the factor of $(1 + b_1 \bar{P})^{-1}$. The actual contribution of the imperfection correction terms to $\ln K_a$ is quite small, amounting to at most only a few percent.

Thermodynamically, we see that GSC may provide a simple method for the determination of adsorption constants; second virial coefficients, depending upon the nature of the system; plus the additional information derivable from these quantities, as from their temperature dependence.

It might be noted that experimental adsorption isotherms are readily obtained by the frontal analysis technique of James and Phillips (22, 31). In addition to being experimentally simpler and faster than conventional methods, this procedure is especially suited to the measurement of very low adsorptions (surface areas $0.25 \text{ m}^2/\text{g}$ or less).

Since deviations from adsorption linearity are due even at very low sample pressures, largely to adsorbent inhomogeneities, it is anticipated that graphitized carbon black will be a valuable adsorbent for experimental studies in GSC. These active solids are prepared by heating carbon blacks to about 3000°C , which causes a crystallization to small graphite polyhedra with a very homogeneous surface of $6 - 30 \text{ m}^2/\text{g}$ (21, 24). Specially modified

adsorbents, such as NaOH-treated Al_2O_3 (34), also possess apparently homogeneous surfaces, and produce linear isotherms.

If high column pressures and decidedly nonideal carrier gases are used, highest accuracy requires the use of the nonideal carrier gas compressibility factor (29), rather than j factors, for the calculation of mean column pressures.

Let us first consider the measurement of thermodynamic quantities by GSC. The reliability of the results obtained with the aid of these equations depends on the extent to which the various cases studied here faithfully describe the physical systems under consideration, and on the validity of the assumptions made concerning these systems. From the slopes of plots of $\ln K_a$, or $\ln k_a$, vs \bar{P} , the mean column pressure, we can extract second virial coefficients for several of the real systems considered. There are definite limitations on the generality of the method.

Obviously, in Case V, the major pressure dependence of K_a lies in the "constant" term, in the factor of $(1 + b_1 \bar{P})^{-1}$. This will make accurate measurements on the nonideality of the gas phase virtually impossible. Thus for these purposes, we must avoid conditions which lead to nonlinear adsorption of the carrier gas; certain carrier gases are eliminated from useful consideration. This is an immediate limitation.

Case III, where the carrier gas is considered ideal, will only hold, and then only approximately, for He carrier gas, which is not ordinarily adsorbed. In this case, we can extract from the retention data values of B_{22} , the second virial coefficients of the pure sample adsorbate vapors. Other information can be obtained from systems described in Cases II and VII. Recall that here the carrier gas is either not adsorbed, or is adsorbed linearly, respectively. Case II will be most applicable at ordinary chromatographic temperatures with H_2 carrier gas; other carrier gases may be

used at higher column temperatures. Systems involving heavier gases at lower temperatures can best be treated as examples of Case VII. The slope of the $\ln K_a$ vs \bar{P} plot provides values of B_{12} for Case II, and $(2B_{12} - B_{11})$ for Case VII. Used conjunctively, we have a potential method for the determination of both quantities. Two different adsorbents of different activities are required. If Case II describes sample retention for the lower activity solid phase, and Case VII that for the more active adsorbent, we can determine both B_{12} and B_{11} . Alternatively, we can obtain B_{12} from GLC measurements⁹ and then apply Case VII. Thus, two columns are required, either two adsorbent columns of different activity, or one with an adsorbent and one with an adsorbent fixed phase. Since we are measuring gas phase interactions, the nature of the column materials in either case should not be critical, for all practical purposes. This is a major advantage of the chromatographic method, in addition to its simplicity and speed.

Previous experimental studies in GSC have generally considered the gas phase ideal; however, these investigations have been more concerned with the theory of adsorption itself,¹⁹ with a detailed description of the chromatographic process and resulting peak shapes,^{10,13} or with column efficiency in GSC.^{12,18}

Adsorption constants can be recovered directly from the measured K_a , or from the intercept of the $\ln K_a - \bar{P}$ plot, depending upon the desired accuracy. As in the measurement of activity coefficients in GLC, extrapolation to zero mean column pressure will be necessary if carrier gases exhibiting nonideal behavior are used.

Barrer and Rees² calculated standard thermal entropies and energies of adsorption from experimentally determined Henry's law constants. Linear relationships were found to exist between these quantities (or their logarithms)

and the covolume, the polarizability, and the force constant of the adsorbed species. A theoretical basis for these observations has been given by Barker and Everett,¹ and Steele and Halsey.³⁵ Gas-solid interaction potentials have also been measured chromatographically.^{19,20} Theoretical calculation of k_H and measurement of K_a allows determination of solid surface areas (equation 10) which are in agreement with values determined with the electron microscope.^{1,20} GSC retention data has also been used to calculate heats of adsorption (equation 6).^{8,16,18}

It has been observed by Greene and Roy¹⁵ that different carrier gases have a marked effect on the retention time of a given adsorbate on a given adsorbent. Table II gives their data, plus an assumed value of k_a and a relative value of b_1 , calculated from their data as discussed below. This behavior can be attributed to the fact that the adsorption of carrier gas reduces the adsorbent area available to the sample vapors, as was discussed above. This is most easily seen if we assume Case IV holds for these systems. Here, $k_a = c_2 RT/Vg (1 + b_1 P)$. All else being equal, the only quantity in the above equation dependent upon the nature of the carrier gas is b_1 , the adsorption constant of the carrier gas. As the degree of adsorption of carrier gas increases, b_1 increases, and k_a decreases. If values

TABLE II

Effect of Carrier Gas on the Retention Time of Methane

<u>Carrier Gas</u>	<u>t_R^1 (min)</u>	<u>k_a^2</u>	<u>b_1^3</u>
Helium	34	16	0
Argon	22	10	0.30
Nitrogen	16	7	0.64
Air	15	6.5	0.73
Acetylene	5	1.5	4.83

¹Retention times of CH_4 on 10 foot charcoal column at 25°C .
Flow rate of carrier gases, 70 cc/min.

²Calculated from $k_a = t_r/t_m - 1$, assuming $t_m = 2$ min.

³Values based on $b_1(\text{He}) = 0$. See text,

of b_1 are known, quantitative prediction of retention behavior follows. Conversely, relative values of b_1 can be calculated from the partition ratios (or retention times) of some compound on a given adsorbent, using different carrier gases at constant temperature and \bar{P} . If one value of b_1 is known independently, or can be measured by other chromatographic experiments (as in Case VIII with He carrier gas and very small samples of the compound of interest such as Ar, N_2 , C_2H_2 , etc.), then we can compute the others.

For example, using Greene and Roy's data,¹⁵ assuming $t_m = 2$ min (this cannot be clearly determined from their paper), we first calculate the values of k_a listed in Table II. Assuming $\bar{P} = 1.5$ atm., $b_1(\text{He}) = 0$ (not adsorbed), and $V_g = 140$ cc, neglecting gas imperfections, we find $c_2 = 0.092$. Using these values, we calculate the relative values of b_1 found in the Table for the various carrier gases, based on $b_1(\text{He})$. Unfortunately, insufficient data are available in the literature to check these numbers.

GSC thus provides a simple, rapid, and probably accurate method for the determination of several quantities of thermodynamic interest.

An important parameter in analytical gas chromatography is the resolving power of the column, expressed as the resolution, R_s , of two closely-eluted compounds of interest, defined here as the ratio of the difference in retention times, $t_{r2} - t_{r1}$, to the standard deviation, σ ,

of one of the peaks, assuming $\sigma_1 = \sigma_2 = \sigma$. It is readily shown that

$$R_s = \sqrt{N} \left[\frac{k_2 - k_1}{1 + k_2} \right] = \sqrt{N} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k_2}{1 + k_2} \right) \quad (38)$$

where N is the number of theoretical plates generated by the second (later) component, and α is the relative retention, k_2/k_1 . From equation 38, and the equations given in Table I, it follows that resolution in GSC is given by the expressions below for the representative systems described in Cases I, IV, and VI.

$$\text{Case I: } R_s = \sqrt{N} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k_H^A}{k_H^A + V_G^0/RT} \right), \text{ etc.} \quad (39)$$

The adsorption constants refer to those of the compound of longer retention time, labeled here as number 2.

It is apparent that approximately similar N will be required to effect the same resolution in Cases I and VI as in GLC. However, Giddings¹² has predicted greater efficiencies for GSC columns. In Case IV, resolution is a function of the nature of the carrier gas and of the mean column pressure, as is retention. For systems with nonlinear isotherms, resolution will decrease somewhat with increasing pressure. Physically, this can again be rationalized in terms of the increased carrier gas adsorption reducing the adsorption sites available to the sample molecules.

The correction factors for gas phase nonideality will affect resolution through both k_a and α . Since this change in retention is dependent not only on the nature of the carrier gas and the mean column pressure, but to some extent also on the structure of the sample molecules, subtle differences in k_a and α can often provide sufficient change in R_s to allow a difficult separation to be made.^{9,14} This effect will

be especially noticeable when capillary columns are used. It is far simpler to change the carrier gas or the mean column pressure than to change the adsorbent to achieve a separation.

GSC also promises to have far wider application to the separation of isotopes than GLC. Using as an example Case IV or VI, the relative retention is

$$\alpha = K_2/K_1 = c_{22}/c_{21} = n_{m2}^2 b_{22}/n_{m1}^2 b_{21} = b_{22}/b_{21} \quad (40)$$

From kinetic gas theory,⁴ b_2 has been given as

$$b_2 = \frac{\int_0^\infty e^{-\Delta H_a/RT} \frac{d\theta}{d\theta} d\theta}{k_0 (2\pi MRT)^{1/2}} \quad (41)$$

where \int_0^∞ is the accommodation (or sticking or condensation) coefficient of the adsorbate on the bare adsorbent surface, ΔH_a is the heat of adsorption, k_0 is an evaporation rate constant, and M is the molecular weight of the adsorbate. Assuming $\alpha_{02} \approx \alpha_{01}$, $k_{02} \approx k_{01}$, and $\Delta H_{a2} \approx \Delta H_{a1}$, $\alpha \approx \sqrt{M_1/M_2}$ (42)

In GLC, if an appropriate liquid could be found for this purpose, (e.g., Cf. reference 6)

$$\alpha = \gamma_2 p_2^0 / \gamma_1 p_1^0 = p_2^0 / p_1^0 \quad (43)$$

where γ_i is the activity coefficient of the solute in the stationary liquid phase and p_i^0 is the vapor pressure of the pure solute.

As an example, consider the chromatographic separation of N_2^{14} and N_2^{15} . The vapor pressures at the triple point are 94.01 and 93.87 mm Hg, respectively.⁷ Thus for GLC, $\alpha = 94.01/93.87 = 1.0042$. For GSC, however, $\alpha = \sqrt{30/28} = 1.0351$. For reasonable retention times, $k = 0$, $R_s = \sqrt{N} [(\alpha - 1) / \alpha]$. If say 98% resolution is desired,

$R_g = 4$, the required number of theoretical plates is about $N = 930,000$ for the GLC column and about $N = 14,000$ for the adsorbent column. Assuming a HETP of 1 mm, the GLC column would have to be about 930 m long (over a half mile) while we would need a GSC column only 14 m long. While these values are approximate, they do give some further idea of the analytical potential of GSC.

Summary

The retention behavior of several defined gas-solid chromatographic systems has been predicted. Sample retention is linearly related to the mean column pressure, decreasing slightly with increasing pressure of non-ideal carrier gases, even in the simplest systems. In the limiting cases of gas phase ideality, the distribution coefficient per unit weight of adsorbent is proportional to the sample adsorption constant. No presumptions are made as to the nature of the interactions which give rise to adsorption; rather, the systems considered are classified according to their observed behavior in terms of the sample and carrier gas adsorption isotherms. The equations presented here are thus restricted to those systems as can be described by the isotherms discussed in this paper. The treatment is, however, readily extended to other types of isotherms.

Considerable potential is seen for the extraction from GSC data of second virial coefficients, adsorption constants, and quantities calculable from these parameters. Analytically, it may be possible to exploit small changes in sample retention arising from gas phase interactions to help effect difficult separations. Gas-solid chromatography also appears to provide a more powerful isotope separation technique than gas-liquid chromatography.

Unfortunately, sufficient data appropriate for testing the theory presented here has not been given in the literature. Experimental studies to this end are therefore being undertaken in this laboratory.

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